LANL Glassy Polymer Model

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This highlight summarizes the development of the GAP model, which is currently being implemented in the LLNL ALE3D code and the SNL CTH code, and has been transitioned to several DoD laboratories for use in their design codes. It is being used at LANL to address polymer-related issues.

Presently, material parameters have been determined for the polymers KelF-800, PTFE, PEEK, PC, Epoxy, and PMMA. While the present model bears very little resemblance to the model of the early years, it originated because of LANL's need to have a continuum model for many National Nuclear Security Administration (NNSA) polymers that operate in their glassy state. Facilitated by the Department of Energy/Department of Defense (DOE/DoD) Joint Munitions Program (JMP), the concept of having a quantitative model for glassy polymers was attractive to several DoD organizations, especially the Army research labs.

The additional incentive of DoD interest accelerated the development of the model in areas related to high-rate impact. While the deformation was not necessarily large, the loading rates and temperatures of interest varied widely from application to application. To have the necessary flexibility to capture the correct thermodynamic behavior in many possible load scenarios, a complete temperature- and pressure-dependent free energy for the volumetric response was deemed to be a necessary component to the model. From a combination of literature- and LANL-measured ambient pressure specific heats and dilatometry data on the specific volume, a semi-empirical equilibrium-specific Gibbs free energy was calibrated for the polymers of interest. For applications within the calibration regime, this allowed for full usage of thermo-mechanical quantities including isothermal bulk modulus, specific heat at constant pressure, and thermal expansion. Figure 1 shows the equilibrium-specific volume and heat capacity for an epoxy resin.

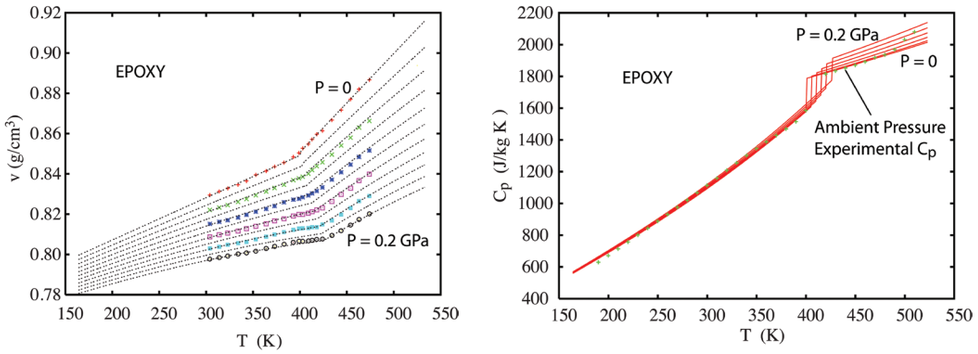

Fig. 1. Equilibrium-specific volume (left) and specific heat (right) from GAP. Experimental points are measured by Dana M. Dattelbaum (WX-9) and Edward B. Orler (MST-7).

Many glassy polymers are known to "flow plastically" by demonstrating a stress plateau, followed by stress softening, finally followed by stress hardening. What is in stark contrast to many other materials (for example, ceramics) is that the stress softening appears to be unrelated to damage. In transparent polymers, for example polycarbonate, stress softening in the stress-strain behavior does not produce visible signs in the polymer, such as whitening–which is often seen as polymer craze and is a clear onset to damage. The mechanisms of polymeric flow and damage at the molecular level are probably related, but this is immaterial for our continuum model, and in the glassy amorphous polymer (GAP) they will be treated as distinct phenomena. Thus a flow stress model has been devised for glassy polymers to handle this behavior. In the GAP model, the flow stress model acts only on deviatoric stress components–an assumption, but one that no available data seems to contradict. Together with a concurrently developed polymer flow stress model, a standard implementation of a generalized Maxwell deviatoric viscoelasticity model, and the equilibrium treatment of the equation of state (EOS) via the Gibbs free energy, stress-strain curves for a variety of glassy polymers were determined for a wide range of rates and temperatures. An example of the GAP stress-strain curves is shown in Fig. 2.

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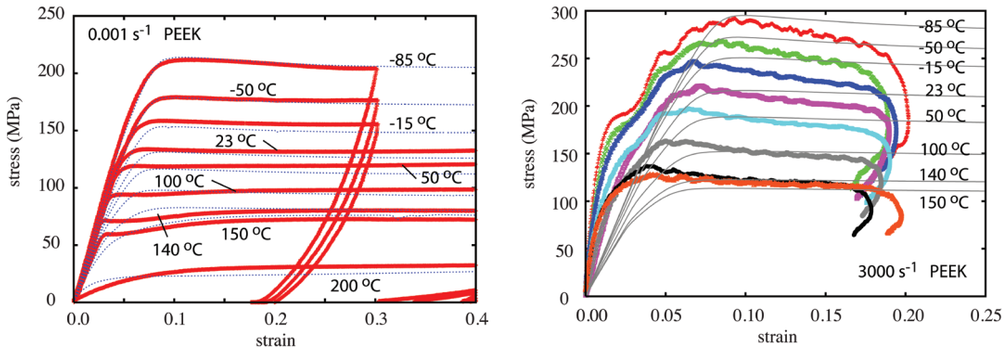

Fig. 2. GAP model stress-strain curves for PEEK at low rates (left) and high rates (right). Measurements are by Phillip Rae (WX-6) and Eric Brown (P-23).

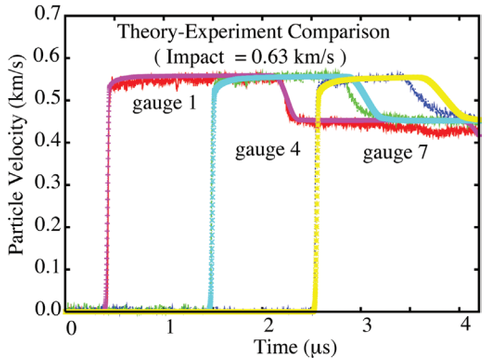

Fig. 3. GAP model shock velocity profile for Kel-F 800. The data are from Dana M. Dattelbaum (WX-9).

Following this work, an important observation was made that altered the direction of GAP development. Because the equilibrium Gibbs free energy was a complete equation of state, all equilibrium quantities, including the Hugoniot, could be calculated. The Hugoniot is the locus of points in thermodynamic space that satisfy the Hugoniot-Rankine jump conditions. The first major upset in releasing GAP for general use occurred when it was realized that the Hugoniot calculated from the equilibrium Gibbs free energy, which was based on equilibrium-measured experimental quantities, did not agree with the high-rate-shock-measured Hugoniot. In fact, the Hugoniot intercepts from the two different methods for some polymers differed by nearly a factor of two when plotted in the Us-Up plane. To a certain degree this discrepancy had been anticipated, however. Considerable literature exists discussing the possibility of volumetric viscoelasticity in polymers. The incorporation of volumetric viscoelasticity was needed in the model to span rates ranging from equilibrium (essentially zero rate) to shock loading rates of 106 to 108 s^{-1}. It happened that since many applications do not span volumetric strain rates that vary from very low to very high, volumetric viscoelasticity may be safely disregarded in those cases. Because the intention of GAP is to be robust enough the handle a variety of loading scenarios (for example those found in an impacted polymer), volumetric viscoelasticity could not be omitted in the model. The final development in GAP was thus the inclusion of volumetric viscoelasticity. Figure 3 illustrates that GAP now captures the correct shock response. Because of the ambiguity in linking the equilibrium EOS with the non-equilibrium behavior, a non-equilibrium free energy approach was developed to provide an unambiguous path forward. The resulting equations derived from the non-equilibrium free-energy-based analysis comprise the current GAP model.

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